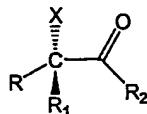
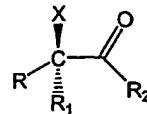


Claims

1. A process for the catalytic asymmetric synthesis of an optically active compound of the formula (1a) or (1b)



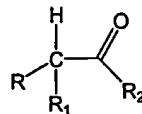
5 (1a)



(1b)

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wherein R is an organic group; X is halogen; R₁ and R₂ which may be the same or different represents H, or an organic group or R₁ and R₂ may be bridged together forming part of a ring system; R and R₂ may be bridged together forming part of a ring system; with the provisio that R and R₁ are different and R₂ when different from H is attached through a carbon-carbon bond, comprising the step of reacting a compound of the formula (2)



15 (2)

with a halogenating agent in the presence of a catalytic amount of a chiral nitrogen containing organic compound.

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2. The process according to claim 1 wherein R₂ is H or an optionally substituted C₁₋₁₀ alkyl group or R and R₂ are bridged together forming part of a ring system.

3. The process according to claim 1 or 2 wherein R₁ is H or an optionally substituted C₁₋₁₀ alkyl group.

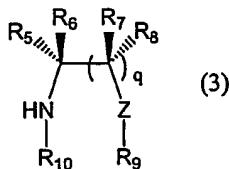
4. The process according to any of the preceding claims wherein R is an optionally substituted C₁₋₁₀ alkyl group, an optionally substituted C₂₋₈ alkylene group or a C₁₋₃-alkylaryl group.

25 5. The process according to claim 4 wherein R is an optionally substituted C₁₋₆ alkyl group, an optionally substituted C₂₋₄ alkylene group or a C₁₋₂-alkylaryl group.

6. The process according to claim 4 or 5 wherein R₁ and R₂ are H.

7. The process according to claim 1 wherein the chiral nitrogen containing organic compound is selected among compounds having a primary or secondary nitrogen atom or when appropriate in one of its salt forms.

8. The process according to claim 7 wherein the chiral nitrogen containing organic compound is selected among compounds of the formula (3)



wherein q is 0 or 1;

R₅, R₆, R₇, R₈, which may be the same or different represents H, alkyl, haloalkyl, alkoxy, OH, amino, amide, silyl, silyl ether, COR₁₁, optionally substituted aryl, an optionally substituted heterocycle, alkyl substituted with at least one OH group, an optionally substituted amino group or optionally substituted aryl or heterocycle or R₅ and R₆ together or R₇ and R₈ together may represent a carbonyl group or when q is 1, R₅ with either R₇ or R₈ may be bridged together forming part of a ring system; R₁₁ represents an optionally substituted amino group or OR₁₂ wherein R₁₂ represents H, alkyl or phenyl;

20 R₉ and R₁₀, which may be the same or different represents H, alkyl, OH, or alkoxy; or R₉ and R₁₀ may be bridged together forming part of a ring system;

Z is S, O, C=O, C(R₁₄)₂, N-R₁₄ wherein R₁₄ is R₅;

with the proviso that the groups R₅, R₆, R₇, R₈, R₉, R₁₀, R₁₄, and Z are selected so that the compound (3) is a chiral compound.

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9. The process according to claim 8 wherein q is 1; R₅, R₆, R₇, R₈ which may be the same or different represents H, COR₁₁, optionally substituted aryl or methyl substituted with at least one of the following, an OH group, an optionally substituted amino group or an optionally substituted aryl or heterocycle group; or R₅ and R₇ together represents a C₃₋₅

alkylene bridge;

R₁₁ represents OH, NH₂ or NH-alkyl;

R₉ and R₁₀ are H or R₉ and R₁₀ together represents a methylene bridge optionally substituted with phenyl, benzyl, COOH or CO-alkoxy;

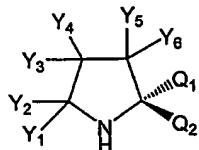
5 Z is CH-R₁₄ or N-R₁₄ wherein R₁₄ represents H or alkyl.

10. The process according to claim 9 wherein either R₅ or R₆ represents H; R₇ and R₈ represents H; R₉ and R₁₀ together represents a methylene bridge and Z is CH₂.

10 11. The process according to claim 3 wherein R₁ is H and R and R₂ each represents an optionally substituted C₁₋₁₀ alkyl group or R₂ together with R forms an optionally substituted C₃₋₅-alkylene bridge optionally with one or more of the carbon atoms being replaced by a heteroatom.

15 12. The process according to claim 1 wherein one or more acids are added to the reaction media.

13. The process according to claim 8, wherein the compound of formula (3) is a compound of formula (4)



(4)

20 wherein Y₁, Y₂, Y₃, Y₄, Y₅, Y₆ which may be the same or different represents H, an alkyl, haloalkyl, an aryl, an alkylaryl, a heterocycle, a halogen, a hydroxyl, a carbonyl, an alkoxy, an ester, an amine, an amide, a silyl, a silyl ether, or Y₂ and Y₃ or Y₄ and Y₅ may be bridged together forming part of a ring system one of Q₁ and Q₂ represent H, alkyl, haloalkyl, alkylaryl and the other the group CY₇Y₈(OY₉) wherein Y₇ and Y₈ which may be the same or different represents alkyl, haloalkyl, an alkylaryl, a heterocycle, or optionally substituted aryl and Y₉ represents a silyl group.

14. A compound of the formula (4) as disclosed in claim 13.

15. The compound according to claim 14, wherein Y_1 , Y_2 , Y_3 , Y_4 , Y_5 , Y_6 each represents H; one of Q_1 and Q_2 represents H; Y_7 and Y_8 each represents an optionally substituted aryl group, wherein the substituents are selected among alkyl and haloalkyl; Y_9 represents tri-alkyl silyl.

16. The compound according to claim 15, wherein Y_7 and Y_8 each represents 3,5-di-trifluoromethyl phenyl and Y_9 represents trimethyl silyl.

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17. The compound according to claim 15, wherein Y_7 and Y_8 each represents 3,5-di-methyl phenyl and Y_9 represents trimethyl silyl.